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| Fundamental molecular, mechanical, and rheological variables driving tribocatalytic processes have been investigated using laser spectroscopic and theoretical modeling studies. These include the use of molecular-optical techniques to probe fluids under high pressure, temperature and shear conditions typical of those encountered in elastohydrodynamic (EHD) lubrication of bearings. In particular, Raman scattering has been used to perform simultaneous <i>in situ</i> measurements of fluid film thickness, temperature, viscosity, and pressure in a model bearing contact. In addition, in order to develop improved models for tribocatalytic phenomena, theoretical (computer simulation and analytical statistical mechanics) and experimental (Raman, fluorescence and picosecond pump-probe) studies have been used to quantitate the effects of high pressure and temperature on molecular rotation, vibration, solvation, isomerization and dissociation. |  |  |
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**Final Technical Report**

**ONR CONTRACT INFORMATION**

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Molecular Optical Probes of Tribological Chemistry  
Under High Pressure, Temperature and Shear

**Performing Organization:**

Purdue University, Department of Chemistry  
Purdue Research Foundation

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**R & T Project Number:**

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**ONR Program Officer:**

Peter P. Schmidt, code 332

## Summary of Significant Results

The following paragraphs and list of publications describe results obtained under ONR-YIP grant no. N00014-92-2559. The PI has received an Innovative Research Award in 1995 for work resulting from this grant, from the Research Committee on Tribology, of the American Society of Mechanical Engineers (ASME).

### 1. Molecular-Optical Sensor Development and Applications.

New molecular-optical fluorescence [*Schrum et al. 1994*] and Raman sensors have been developed and optimized for characterizing thin tribological fluid films. These studies include the design and construction of a microscope based Raman system for direct *in situ* studies of operating tribo-contacts [*LaPlant and Ben-Amotz 1995*]. This apparatus was used to demonstrate a new Raman technique for the measurement of lubricant film thickness on a bearing contact surface [*Hutchinson et al. 1995*]. Work is continuing in molecular-optical sensor measurements of local pressure and temperature in operating tribo-contacts.

In addition to the above tribological applications of our molecular-optical sensors, we have demonstrated a wide range of other important practical application of this technology (see overhead transparencies included with N00014-92-1559 EOFY-95 report). The high molecular information content of Raman scattering shows great promise in industrial process monitoring, quality control, and automated plastic recycling applications [*Ben-Amotz et al 1994*]. Preliminary studies of Raman scattering by objects embedded in highly scattering (interlipid) media, have been used to quantitate the capabilities of Raman in non-invasive biological tissue biopsy and blood chemical analysis [*Thompson et al 1995*].

An important new technological development which has grown out of the above work involves the use of optical fiber bundles to simultaneously achieve both confocal and super-focal collection of optical signals emanating from micro-structured materials. This technique utilizes a fiber bundle which is arranged in a circular geometry at one end, and a linear stack at the other end (see overhead transparencies included with N00014-92-1559 EOFY-95 report). The circular end serves as an adjustable size aperture, while the linear end serves as the entrance slit of a spectrograph. Thus the signal collection depth within a sample is under software control (by selection of readout rows on the spectrograph CCD detector), without any sacrifice in spectrograph resolution. In other words, this technique not only allows remote automated control of signal collection depth, but also circumvents the traditional optical trade-off between collection volume and spectroscopic resolution.

### 2. Modeling Chemical Processes in High Pressure and Temperature Fluids.

The following paragraphs summarize our recent progress experimental and theoretical studies used to develop improved models of chemical processes in high pressure and temperature fluids. Such studies are critical to the fundamental understanding of chemical processes occurring in tribological systems, where chemical equilibria and reaction rates may be perturbed far from their values under ambient pressure and temperature conditions. Our work focuses on modeling fundamental molecular translational, rotational, and vibrational motions of molecules, as well as more complex chemical isomerization and dissociation processes. Note that although not all of the work described below was supported directly by this ONR grant, it is all of relevance to modeling tribocatalytic processes, and thus is closely coupled to this grant project.

### a) Molecular Rotational Dynamics

New picosecond fluorescence depolarization measurements have been combined with an exhaustive survey of previous molecular rotational and translational diffusion results in order to develop improved models for microscopic friction in liquids. A surprisingly general, nearly quadratic, correlation between molecular volume and microscopic viscosity is revealed [Williams, Jiang, and Ben-Amotz 1994]. This correlation allows the prediction of microscopic frictional damping of molecular motions for molecules and molecular subunits ranging in size from small diatomics to large polycyclic aromatic hydrocarbons (PAHs) and biomolecules. Theoretical analysis using hard body fluid kinetic theory and continuum hydrodynamics reveals that this general is closely coupled to the increase in molecular anisotropy with increasing size [Ravi and Ben-Amotz 1994].

### b) Molecular Vibrational Frequency Shifts.

Accurate statistical mechanical expressions for binary solute-solvent intermolecular interaction potentials are used to predict vibration frequency shifts of molecules in gas, liquid, and van der Waals cluster systems [de Souza and Ben-Amotz 1995]. The results are compared with experimental measurements for H<sub>2</sub>-rare gas solutions and clusters. The observed behaviors are found to differ markedly when using the very accurate Leroy-Hutson TT<sub>3</sub> potential as opposed to a standard Lennard-Jones atom-atom additive potential. The more realistic potential not only has a minimum energy and maximum H<sub>2</sub> bond softening in the linear (as opposed to a T) configuration, but it also yields temperature dependent frequency shifts which are in better agreement with experimental results.

### c) Molecular Solvation Thermodynamics

Perturbed hard body fluid theory is used to model molecular solvation free energies in hexane and water [de Souza and Ben-Amotz 1995]. The results allow the separation of attractive and repulsive (packing) contributions to molecular solvation. The results also support a new model for the hydrophobic effect linked to the reduced translational (rather than orientational) mobility of water molecules around a non-polar solute. Monte Carlo computer simulations are used to test hard fluid (HF) model predictions for repulsive (packing) contributions to the chemical potential and solvation force of spherical, diatomic, and polyatomic solutes [de Souza, Stamatopoulou, and Ben-Amotz 1994; Stamatopoulou, de Souza, Talbot and Ben-Amotz 1995]. The results justify approximating small polyatomic solutes by hard spheres in predicting repulsive packing force contributions to solvation thermodynamics.

### d) Molecular Isomerization and Dissociation

Perturbed hard body fluid theory has been used to model the effects of pressure and temperature on isomerization and dissociation reactions [de Souza and Ben-Amotz 1994; de Souza and Ben-Amotz 1995]. These have established practical procedures for extracting repulsive and attractive intermolecular interaction parameters from experimental data. Our results also yield practical algorithms for predicting chemical thermodynamic properties at high pressures and temperatures, where little direct experimental data may be available. A particularly interesting aspect of the results is the prediction of a strong sensitivity of reaction volumes and enthalpies to small changes in intermolecular coupling strength in the supercritical fluid region. This not only explains large changes in chemical reactivity in supercritical fluids, but also suggest the possibility of more accurately determining intermolecular potential functions using supercritical fluid spectroscopic and thermodynamic measurements.

Publications Citing ONR Support  
(grant no. N00014-92-1559)

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